POLYMER CHEMISTRY

AN INTRODUCTION

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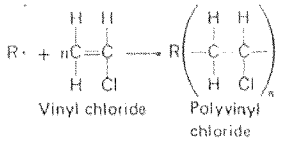
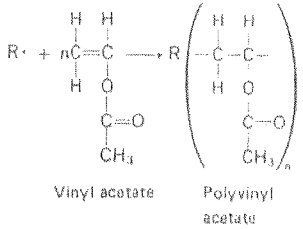


(9.32)

Monomers may also be polymerized in solution using good or poor solvents for homogeneous and heterogeneous systems, respectively. Solvents with low chain-transfer constants should be used whenever possible to minimize reduction in molecular weight. While telogens do decrease molecular weight, the latter and the rate of polymerization are independent of the polarity of the solvent in homogeneous solution systems.

Polyvinyl acetate (PVAc) may be produced by the polymerization of vinyl acetate in the presence of an initiator in a solution such as benzene. The viscosity of the solution continues to increase until the reaction is complete, but the concentration of the solution is usually too dilute to exhibit autoacceleration because of the gel effect. The solution may be used as prepared, the solvent may be stripped off, or the polymer may be recovered by pouring the solution into an agitated poor solvent, such as ethanol.

PVAc is used in adhesives and coatings, and may be hydrolyzed to produce water-soluble polyvinyl alcohol (PVA). The latter, which is produced at an annual rate of 56,000 tons, may be reacted with butyraldehyde to produce polyvinyl butyraldehyde (PVB) (used as the inner lining in safety glass). The equations for the production of these polymers are as follows:



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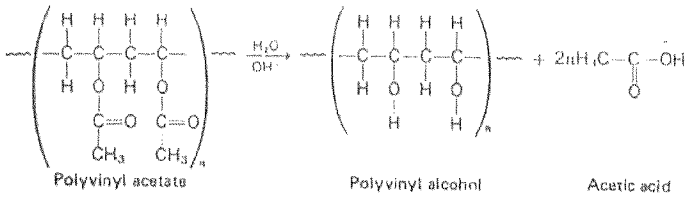
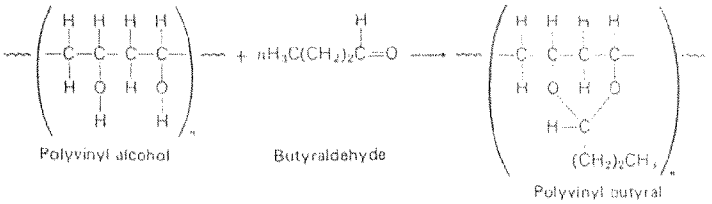
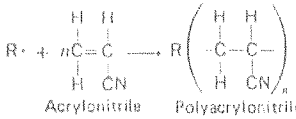


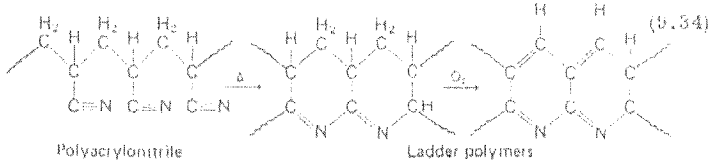


(9.33 cont.)

When a monomer such as acrylonitrile is polymerized in a poor solvent such as benzene, macroradicals precipitate as they are formed. Since these are "living polymers," the polymerization continues as more acrylonitrile diffuses into the precipitated particles. This heterogeneous solution type of polymerization has been called precipitation polymerization. Acrylic fibers (Acrilan; produced at an annual rate of 339,000 tons) are based on polyacrylonitrile (PAN).

Since the acrylonitrile is carcinogenic, precautions must be taken to avoid contact with this monomer. The latter must not be present in high concentrations in acrylic fibers or plastics. It is of interest to note that polyacylonitrile forms a heat-resistant ladder polymer when heated at elevated temperatures. The equations for these reactions are as follows:





(9.34)

The black ladder polymer produced by pyrolysis of PAN is sometimes called black nylon or fiber AF. Polyacrylonitrile is a hydrogen-bonded polymer with a high solubility parameter value, on the order of 15 H, and hence is soluble only in polar solvents such as N,N-dimethylformamide (DMF).

Many water-insoluble vinyl monomers may also be polymerized by the emulsion polymerization technique. This technique, which differs from suspension polymerization in the size of the suspended particles and

in the mechanism, is widely used for the production of many commercial plastics and elastomers. While the particles in the suspension range from 10 to 1000 nm, those in the emulsion process range from 0.05 to 5 nm. The small beads produced in the suspension process may be separated by filtering, but the latex produced in emulsion polymerization is a stable system in which the charged particles cannot be removed by ordinary separation procedures.

Since relatively stable macroradicals are produced in the emulsion process, the termination rate is decreased and a high molecular weight product is produced at a rapid rate. It is customary to use a water-soluble initiator such as potassium persulfate, and an anionic surfactant such as sodium stearate and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40 to 70°C.

A typical recipe for emulsion polymerization includes 100 g of monomer, such as styrene, 180 g of water, 5 g of sodium stearate, and 0.5 g of potassium persulfate. When the concentration of soap exceeds the critical micelle concentration (CMC), these molecules are present as micelles in which the hydrophilic carboxylic acid ends are oriented toward the water-micelle interface, and the lyophilic hydrocarbon ends are oriented toward the center of the micelle. The micelles are present as spheres with a diameter of 5 to 10 nm when the soap concentration is less than 2%. However, with the higher concentrations customarily used, the micelles resemble aggregates of rods which are 100 to 300 nm in length.

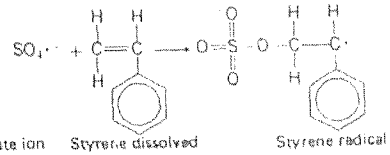
As shown in Fig. 9.3, the water-insoluble monomer is attracted to the lyophilic ends in the micelles, and this causes the micelles to swell. The number of swollen micelles per milliliter of water is on the order of 10^{18}. However, at the initial stages of polymerization (phase I), most of the monomer is present as globules which resemble those observed in suspension polymerization.

Since the initiation of polymerization takes place in the aqueous phase, essentially no polymerization takes place in the globules. Thus, they serve primarily as a reservoir of monomer supplied to the micelles to replace the monomer converted to polymer. The number of droplets per milliliter of water is on the order of 10^{11}. Hence, since there are 10 million times as many micelles as droplets, the chance of initiation of monomer in a droplet is very, very small.

As shown in the following equations, the persulfate ion undergoes homolytic cleavage to produce two sulfate ion radicals. These serve as initiators for the few water-soluble monomer molecules present in the aqueous phase.

$$S_2O_8^{--} \longrightarrow 2SO_4^{\cdot -} \qquad (9.35)$$

Persulfate ion — Sulfate ion radical



(9.35 cont.)

According to a theory proposed by Harkins and refined by Smith and Ewart, the first stages of propagation in an emulsion system also take place in the aqueous phase to produce a more lyophilic surface-active oligoradical, as shown below in (9.36).

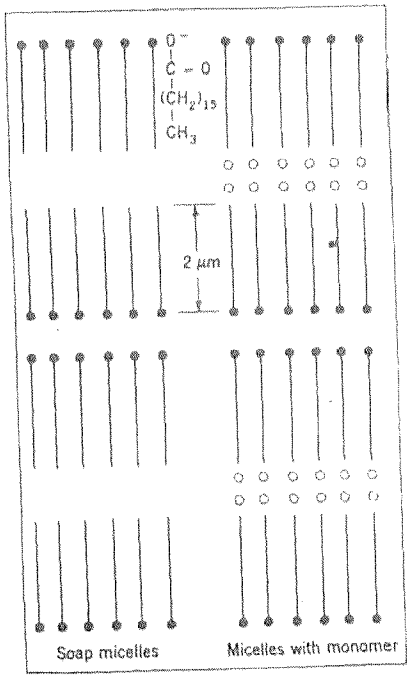


FIGURE 9.3 Micelles swollen with solubilized styrene monomer. (From Introduction to Polymer Chemistry by R. Seymour, McGraw-Hill, New York, 1971. Used with permission of McGraw-Hill Book Company.)